

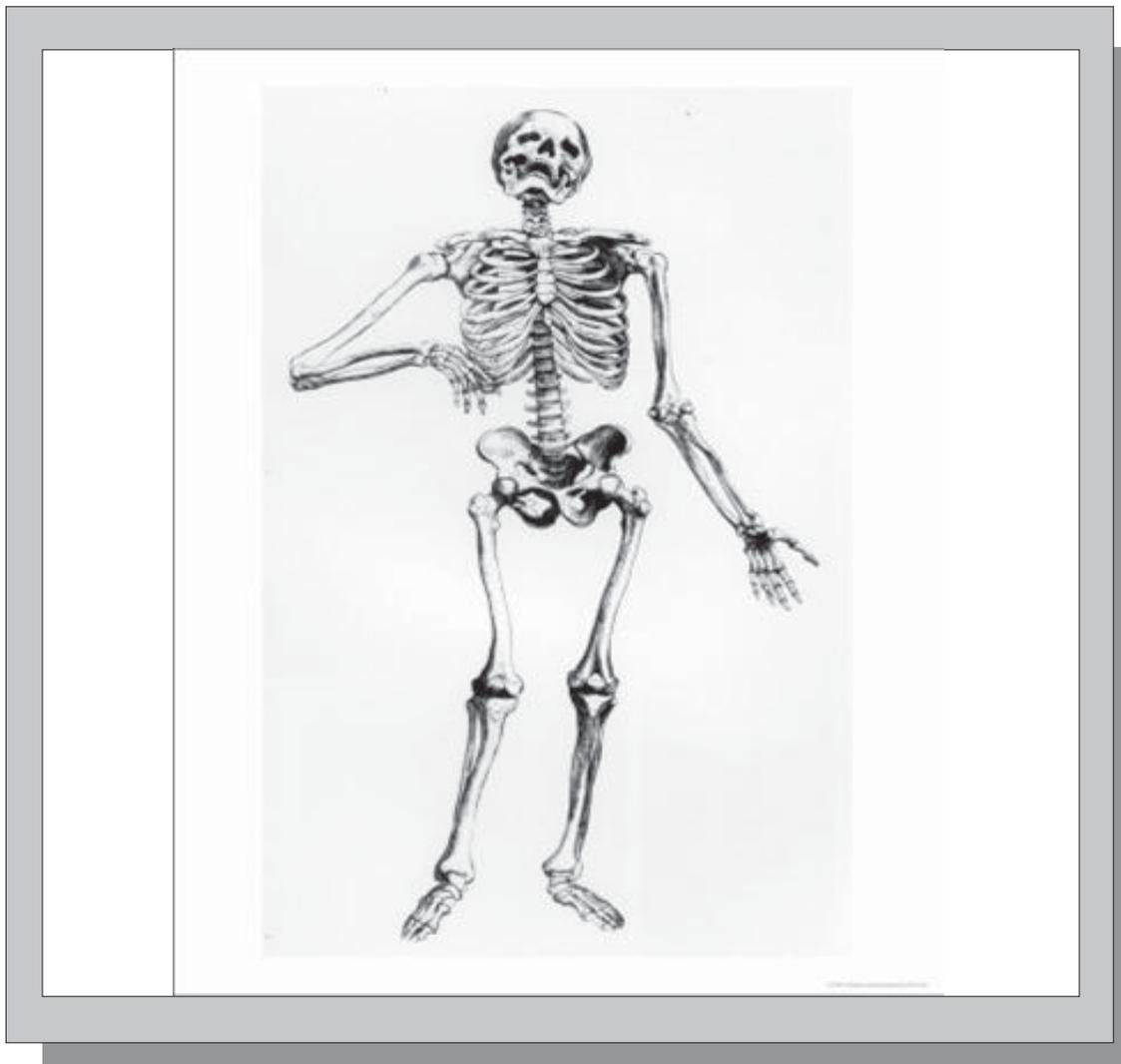


CRIMEScene

Newsletter of the Northwest Association of Forensic Scientists

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PRESIDENT'S MESSAGE**MATTHEW JORGENSON**

I can't believe Labor Day is around the corner (may have passed by the time the newsletter gets to print) and I am sitting down to write my last president's address! What a year it has been. I made a commitment to you at the start of my term and throughout this past year I have tried to reach out to as many of you as I could...through this message, through personal conversations, and through trying to organize a training venue that meets the needs of our organization. I will not even pretend, however, to tell you that this was a task taken on by me alone. I want to take just a minute and give a nod and heart-felt "thank you" to all of the members of this year's Board of Directors, specifically those stepping down after their term of service. Take, for instance, the job of putting together this newsletter - "props" go to Kori Barnum, who has served as Editor of this newsletter and has kept me "on point" throughout the year. I also want to thank the Functional Area Liaisons for taking up the challenge set in front of them and doing such a great job of it. True leadership was shown by our "FAL guys" (sorry – the phrase just HAD to be used) in coming up with training in different disciplines as they followed suggestions that were sought based on input from the membership. Lastly, to the instructors who have stepped up to help continue the craft that you take pride in. Thank you all for your service.

As we gear up for the NWAFS Fall Conference, my hope is that we have listened to the membership and that this organization has served you. On the 21st through the 25th of September our annual training seminar will be held and hosted here in Colorado at the Marriott Inn in Fort Collins. Several workshops dedicated to crime scene processing have been set up – one of which will involve a buried body and another will be on the processing of evidence from arson scenes. We have a serial number restoration class and a class in shotgun pattern analysis. Also, the FBI will be hosting a class in the recognition and analysis of improvised and other explosives involving both class room and field days. There will be a round-robin seminar series on mixture DNA samples put on by experts from around the nation, and an instrumentation class focusing on WHY they are so commonly used in the area of forensic chemistry. This should make for a very robust training seminar and I am very encouraged by the registration numbers. Given how heavily the training budgets from our organizations have been impacted, the planning committee and instructors should take pride that this training is still regarded as salient and worth taking. It speaks volumes as to the commitment our folks have to this organization!

That brings me to what has become my calling card of sorts...it has been the theme for each of the last newsletters, but bears repeating as I close my last address: at the heart of all that we do as forensic scientists, never forget that we are in service to the justice system...and to each other. There are several board positions that will come open this year. There will be opportunities throughout the coming year to be on committees, to serve as a Functional Area Liaison, or to publish in the newsletter. Take the challenge and give to this great organization; you will help steer the direction of its future. Through new blood and new ideas we continue to stay relevant to our profession and to our service agencies. Keep fighting the good fight that we all get up and fight each day, folks. Your services are invaluable and so, too, is your commitment to serve...for that, I thank you.

Matt Jorgenson, NWAFS President

EDITOR'S MESSAGE**KORI BARNUM**

This issue of the newsletter marks my last edition as editor. It has been a privilege to work with such dedicated and innovative scientists, folks who are passionate about their work and committed to helping others in their field. Thank you for your interest and involvement in the NWAFS!

I hope many of you can attend and enjoy the Fall Meeting in Fort Collins - and also join us next year in Portland!

Wishing you all the best -

Kori Barnum

Retiring NWAFS Editorial Secretary

CRIMESCENE is the official publication of the Northwest Association of Forensic Scientists. It is published four times a year in the months of February, May, August, and November. The Newsletter welcomes submissions from its membership, such as: technical tips, case studies, literature compilations, workshop or training notifications, reference citations, commentary, historical accounts, and other topics of interest to the membership. Please submit material for publication in Microsoft Word for Windows format as an e-mail attachment. For more information regarding the Newsletter or to make a submission please contact Kori Barnum at kori.barnum@state.or.us.

Acetylation of Phenethylamines and Substituted Piperazines

Calvin Davis

Forensic Scientist, Oregon State Police

On April 3, 2009, Forensic Scientist Kyle Mitchell and I conducted an investigation of the acetylation of various phenethylamines and substituted piperazines by aspirin (acetylsalicylic acid). This investigation was prompted by the appearance of a 2008 case analyzed by Forensic Scientist Leland Samuelson that contained some "ecstasy" like tablets that appeared to contain aspirin, caffeine, TFMPP (trifluoromethylphenylpiperazine) and BZP (benzylpiperazine). Some unidentified peaks in the spectrum were tentatively attributed to some sort of reaction between the aspirin and the piperazines. Further investigation into the matter yielded the following experiment.

Standards of aspirin, methamphetamine, MDMA (3,4-methylenedioxy-meth-amphetamine), MDEA (3,4-methylenedioxyethylamphetamine), BZP and TFMPP with a concentration of approximately 1 mg/mL were prepared in methanol. From the working solutions, mixtures of differing ratios of aspirin and the other substances were prepared.

Mix 1 – Meth:Aspirin – 25uL:75uL

Mix 2 – Meth:Aspirin – 50uL:50uL

Mix 3 – Meth:Aspirin – 75uL:25uL

Mix 4 – MDMA:Aspirin – 25uL:75uL

Mix 5 – MDMA:Aspirin – 50uL:50uL

Mix 6 – MDMA:Aspirin – 75uL:25uL

Mix 7 – MDEA:Aspirin – 25uL:75uL

Mix 8 – MDEA:Aspirin – 50uL:50uL

Mix 9 – MDEA:Aspirin – 75uL:25uL

Mix 10 – BZP:Aspirin – 25uL:75uL

Mix 11 – BZP:Aspirin – 50uL:50uL

Mix 12 – BZP:Aspirin – 75uL:25uL

Mix 13 – TFMPP:Aspirin – 25uL:75uL

Mix 14 – TFMPP:Aspirin – 50uL:50uL

Mix 15 – TFMPP:Aspirin – 75uL:25uL

Mix 16 – Meth:MDMA:MDEA:BZP:TFMPP:Aspirin – 10uL: 10uL: 10uL: 10uL: 10uL:60u L

Mix 17 – Meth:MDMA:MDEA:BZP:TFMPP:Aspirin – 15uL: 15uL: 15uL: 15uL: 15uL:40uL

Mix 18 – Meth:MDMA:MDEA:BZP:TFMPP:Aspirin – 20uL: 20uL: 20uL: 20uL: 20uL:20uL

These mixtures were subsequently analyzed via GC/MS (gas chromatograph/mass spectrometer) on the PDX-GCMS5975B on the DRUGRAMP method, which is a general screening method for controlled substances. The same mixtures were also analyzed on the same instrument using another method that altered the injection port temperature from 250°C to 200°C, this method was named DRUGRAMP2. The injection port temperature was varied as part of this experiment to observe if lower temperatures in the inlet affected the presence or abundance of substitution products of the acetylation of the phenethylamines and piperazines.

In each of the analyses of the mixtures above, at least one or more of the aspirin breakdown products were seen in the chromatograms. These compounds include methyl salicylate, salicylic acid and aspirin. It was not determined if these products are due to breakdown of aspirin in methanol or the breakdown of aspirin in the GC injection port.

Methyl salicylate: retention time of ~ 3.315 min, m/z 120, 152, 92, 58, 65...

Salicylic acid: retention time of ~ 3.691 min, m/z 120, 92, 138, 64...

Aspirin: split peak/retention time of ~ 4.506 and 4.901 min, m/z 120, 121, 138, 43, 92, 163, 180...

The methamphetamine/aspirin mixtures all yielded a methamphetamine double peak and an acetylated methamphetamine peak in the chromatogram. The split methamphetamine peak is the result of the methamphetamine salt standard (meth HCl) interconverting between the salt and base forms of the compound when dissolved in methanol. Both the base and salt form are seen in the chromatogram. As expected, the ratio of methamphetamine to acetylated methamphetamine was dependent on the original ratio of methamphetamine to aspirin.

Methamphetamine: split peak(s)/retention time of ~ 3.299-3.423 min, m/z 58, 91, 117, 134, 148...

N-acetyl-methamphetamine: retention time of 5.067 min, m/z 58, 100, 91, 43, 117, 134, 148...

All MDMA/aspirin mixtures yielded an MDMA peak and an acetylated MDMA peak in the chromatogram. As expected the ratio of MDMA to acetylated MDMA was dependent on the original ratio of MDMA to aspirin.

MDMA: retention time of ~ 4.812 min, m/z 58, 135, 77, 51, 191...

N-acetyl-MDMA: retention time of ~ 6.384 min, m/z 58, 162, 100, 135, 77, 43, 235...

All MDEA/aspirin mixtures yielded an MDEA peak and a minor acetylated MDEA peak in the chromatogram. Unexpectedly, the ratio of MDEA to acetylated MDEA was not dependent on the original ratio of MDEA to aspirin. Acetylated MDEA was a minor product of the reaction in all mixtures. One hypothesis is that the ethyl group causes steric hindrance in the replacement of the hydrogen on the amine nitrogen of MDEA, compared to the smaller methyl group on the amine nitrogen of MDMA, which is readily acetylated.

MDEA: retention time of ~ 4.999 min, m/z 72, 44, 135, 77, 105, 206...

N-acetyl-MDEA: retention time of ~ 6.520 min, m/z 72, 162, 114, 135, 207, 77, 43...

All BZP/aspirin mixtures yielded an acetylated BZP peak in the chromatogram. The mixture with the highest concentration of aspirin yielded no BZP peak in the chromatogram. The other two mixtures of lower aspirin concentration had a BZP peak in the chromatogram. As expected the ratio of BZP to acetylated BZP was dependent on the original ratio of BZP to aspirin. The full acetylation of BZP in the presence of excess aspirin may be due to the fact that the hydrogen on the cyclic amine is highly sterically available for replacement by the acetyl group.

BZP: retention time of ~ 4.656 min, m/z 91, 134, 176, 56, 65, 120...

N-acetyl-BZP: retention time of ~ 6.372 min, m/z 91, 146, 134, 132, 85, 175, 218...

All TFMPP/aspirin mixtures yielded an acetylated TFMPP peak in the chromatogram. The mixture with the highest concentration of aspirin yielded a very small TFMPP peak in the chromatogram. The other two mixtures of lower aspirin concentration had a significant TFMPP peak in the chromatograms. As expected the ratio of TFMPP to acetylated TFMPP was dependent on the original ratio of TFMPP to aspirin. The significant acetylation of TFMPP in the presence of excess aspirin may be due to the fact that the hydrogen on the cyclic amine is highly sterically available for replacement by the acetyl group.

TFMPP: retention time of ~ 4.788 min, m/z 188, 230, 172, 145...

N-acetyl-TFMPP: retention time of ~ 6.361 min, m/z 200, 188, 272, 172, 145, 56, 229, 253...

All meth/MDMA/MDEA/BZP/TFMPP/aspirin mixtures yielded methamphetamine, MDMA, and MDEA peaks in the chromatograms. Very small acetylated methamphetamine peaks existed in the mixtures with higher aspirin concentration. No acetylated MDEA was present in any of the chromatograms. The acetylated products of MDMA, TFMPP and BZP appear to all co-elute in one peak at approximately 6.371 minutes in the chromatogram. The mixture with the highest aspirin concentration showed evidence of the acetylated products of MDMA, TFMPP and BZP in this peak. The mixtures with the lowest two aspirin concentrations showed evidence of only the acetylated products of TFMPP and BZP in the chromatogram. This suggests that TFMPP and BZP are preferred reactants with aspirin versus MDMA, methamphetamine and MDEA. This fits the hypothesis of the hydrogen on the cyclic amines of the piperazines being highly sterically available as opposed to the hydrogen on the nitrogen of the phenethylamines. As expected, the ratio of the phenethylamines and piperazines to acetylated products thereof was dependent on the original ratio of these compounds to aspirin.

TFMPP: retention time of ~ 4.788 min, m/z 188, 230, 172, 145...

N-acetyl-MDMA, N-acetyl-BZP and N-acetyl-TFMPP: retention time of ~ 6.371 min, m/z 91, 146, 134, 132, 200, 188, 175, 218, 272...

All of the mixtures were run on DRUGRAMP2 with the same conditions except for the variance of the injection port temperature. No significant differences were noticed in the chromatograms when the injection port temperature was changed. Therefore, no inferences can be made regarding the influence of temperature and the reaction of aspirin with secondary amines. Acetylation may occur upon dissolution in methanol, or it may happen upon injection into the GC injection port. Further work would have to be performed to investigate this reaction.

In summary, in the presence of aspirin or compounds with the ability to donate an acetyl group, primary or secondary amines may be subject to acetylation when the mixture is dissolved in methanol and analyzed by GC/MS. Analysts should be aware of the potential for unknown peaks if evidence containing a mixture of one or more of the piperazines or phenethylamines exists with aspirin, and is subsequently extracted with methanol. Furthermore, analysts should be aware that acetylated products of MDMA, BZP and TFMPP may co-elute under standard analysis conditions on the GC/MS. A base into hexane extraction will remove the aspirin and reduce the risk of acetylation of the compounds of interest.

The author would like to acknowledge the Oregon State Police Forensic Services Division for the use of equipment, materials and the opportunity to conduct this research.

NOTICE TO NWAFS MEMBERSHIP:

The SWGDRUG core committee currently has two pending documents out for review by the forensic science community. To ensure the documents address the needs of the community, SWGDRUG invites Northwest Association of Forensic Scientists (NWAFS) members to comment and offer suggestions. Comments and suggestions should be submitted by September 30, 2009.

Pending Documents:

- 1) SWGDRUG has reviewed the published SWGDRUG Recommendations and made a number of revisions. These revisions harmonize terminology, correct grammar, add references, link sections and clarify recommendations as appropriate. All changes are written in red text.
- 2) In addition, SWGDRUG has prepared a new Supplemental Document SD-3 which provides examples of the estimation of uncertainty of measurement in weight determinations.

NWAFS members are invited to review these documents
and send comments to swgdrug@...

These documents can be found in the pending documents section on the SWGDRUG website, <http://www.swgdrug.org/pending.htm>.



A Sampling of the Criminally Stupid....

He's Hoppin' Mad

In Pomona, CA, a burglary suspect was caught when his artificial leg fell off as he was attempting to flee.

O Brother, Where Art Thou?

In DeQueen, Arkansas, a man who was arrested for DUI and identified himself as his brother, seeking to keep the arrest off his record, then called the same brother to come down to the police station to bail him out.

But I Heard You Had a Crack Loan Department!

In Callaway, FL, a man went to his bank and told the loan officer that he needed a \$500 loan to pay off a crack cocaine debt to another man who was waiting for him in the bank's lobby. Both men were arrested.

Can't Foot the Bill

After Marshall Wolbers, 56, was arrested for skipping out on paying for services at nearly two dozen spas in the Chicago area, one pedicurist said: "I just want to look at him like, 'You jerk, you didn't even tip me. You made me rub your gross feet and listen to you for an hour and a half'".

The Daily Doofus

Today's doofus robbed a Wendy's restaurant in Miami, wearing a bandanna to cover his face. During the heist, however, his bandanna kept falling off, revealing a very recognizable tattoo of a tear on his cheek. Then, four days later, he came back to the same Wendy's and ordered three bacon cheeseburgers from the same cashier he'd robbed, even arguing with the clerk about the amount of change he was given. He was arrested.

Taken from *The Oregonian*, April 16, 2007

The NWAFS now has the ability to accept Paypal!

When registering for the September 21-25, 2009 NWAFS Meeting, go to www.nwafs.org and use the “Pay Your Registration Now With PayPal” button.

Please let either Robbie Heegel or Jeff Borngasser know if you experience any problems using PayPal to pay for your meeting registration.